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<p>(54) Title: THE USE OF NATURAL OILS IN HOT MELT ADHESIVES</p>		
<p>(57) Abstract</p>		
<p>A process for bonding tissue or nonwoven to similar or dissimilar substrates comprising the step of applying to at least one substrate a molten hot melt adhesive composition, said hot melt adhesive containing, as the plasticizing agent, a hydrogenated or non-hydrogenated natural oil selected from the group consisting of fatty acids containing about 6 to 22 carbon atoms and the pure fatty acid fragments thereof.</p>		

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**THE USE OF NATURAL OILS IN HOT MELT ADHESIVES****BACKGROUND OF THE INVENTION**

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Hot melt adhesives are used commercially for a wide variety of applications. The major advantage of hot melt adhesive systems is the lack of a carrier fluid which eliminates the need for drying the adhesive film once it is applied to the substrate. This elimination of the drying step overcomes hazards associated with solvent usage and also allows for faster production line speeds and lower transportation costs.

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These hot melt adhesives have historically been based on petroleum derived polymers such as polyethylene, ethylene-vinyl acetate, styrenic block copolymers and polypropylene. Water sensitive hot melts have also been prepared from vinyl pyrrolidone polymers including vinyl acetate/vinyl pyrrolidone copolymers. All these adhesive compositions are further tackified, plasticized and/or reinforced with a variety of resins, oils and/or waxes which are derived from both petroleum and naturally occurring feedstocks such as wood, gum and tall oil rosin and terpenes. In particular, these adhesives generally utilize plasticisers based on hydrocarbon oils which may be described as paraffinic, naphthenic or aromatic depending upon the relative number of carbon atoms. These classic compositions suffer from the cyclical price cycles common to all oil derived materials and also are generally very resistant to degradation once the articles employing them are disposed of.

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Moreover, most commercially available hot melt adhesives, including those containing vinyl pyrrolidone and other polymers as discussed above, require temperatures of 160-180°C or greater to ensure complete melting of all the components and also to achieve satisfactory application viscosity. The need for such elevated temperatures is not without problems. Thus, the high temperatures increase the operator's risks with respect both to burns and to inhalation of residual volatiles. Finally, the high temperatures require more energy, placing greater demands on the manufacturing facility.

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There is also an increasing demand for hot melt adhesives which can be applied at low temperatures so as not to damage certain heat sensitive substrates on which they are coated. For example, in the case of construction of disposable diapers, the adhesive

is often coated onto the thin polyolefin substrate which provides the moisture barrier. Such substrates may be readily deformed or even melted by the application of conventional hot melt adhesives which must be heated to temperatures of about 160°C in order to become sufficiently molten for application. In such cases, the viscosity of the adhesives must be low enough and the set speed fast enough to give good machinability, for example, on automatic equipment with short compression sections. The thermal stability and aesthetics also must be such as to produce no charring, skin, or gel formation coupled with a small viscosity change following prolonged aging at typical operating temperatures (e.g. 180°C) so as to minimize down time for maintenance and to provide consistent application patterns and amounts during operation. These aesthetic considerations have become more important in recent years as customers increasingly demand hot melt adhesives having pot clarity, i.e. adhesives which are clear in their molten form.

While the use of vegetable oils has been generally alluded to in the past, these oils were not generally used in the industry and certainly not recognized as providing any benefit with respect to properties required in conventional labelling or nonwoven applications.

#### SUMMARY OF THE INVENTION

We have now found that the substitution of natural oils, such as hydrogenated or non-hydrogenated natural oil or the pure fatty acid fragments thereof, for hydrocarbon oils in a wide variety of hot melt adhesive systems provides adhesives with desirable physical properties of low softening point and viscosity without the corresponding reduction in adhesion properties which generally accompany the low softening, low viscosity systems. Thus, not only are the compositions of the present invention novel, but when specifically formulated, they may be characterized by sufficiently low coating viscosities (i.e. about 900 - 3,000 mPa s at 130°C) so as to enable application at very low temperatures (i.e. about 100°C) while still maintaining a high level of heat stress resistance. As an additional advantage, the low coating temperature provides a substantial reduction in the level of

volatiles released into the manufacturing environment during use. In addition, the use of certain natural oils imparts a superior degree of thermal stability manifesting as a reduced level of viscosity change after aging as well as superior color. Further, the resultant adhesives are characterized by long open times with extremely good penetration into the substrate being coated. Finally, the fact that a large portion of the components are derived from natural products provides for a more environmentally friendly product.

The specific oils contemplated for use herein are the hydrogenated or non-hydrogenated natural oils comprising fatty acids containing about 6 to 22 carbon atoms as well as the pure fatty acid fragments thereof. Particularly preferred for use herein are C10-C14 blends such as such as coconut oil, as well as C18 blends such as soybean and sunflower oils. Depending upon the viscosity desired in the final adhesive, the natural oil may be added in amounts of about 5 to 30% by weight with the lower amounts providing higher viscosity. Thus, for adhesive compositions which are characterized by lower viscosity at the lower coating temperatures, amounts of about 20 to 30% by weight are preferred.

The natural oils may be used in conjunction with virtually any hot melt adhesive used in disposables applications including, but not limited to, those hot melt adhesive compositions based on ethylene/vinyl acetate copolymers, isotactic or atactic polypropylene, styrene-butadiene, styrene-isoprene, or styrene-ethylene-butylene or styrene-ethylene-propylene A-B-A or A-B-A-B block copolymers or mixtures thereof. If used as the base component in a hot melt adhesive, the block copolymer is usually present in an amount of 10 to 30% by weight of the adhesive. In addition to the base polymer, these hot melt adhesive compositions generally contain tackifiers, oils and/or waxes as well as conventional additives including stabilizers, anti-oxidants, pigments and the like. Typical of such formulations are those described in US Patent Nos. 4,460,728 issued July 17, 1984 to R. C. Schmidt, Jr. et al.; 3,492,372 issued January 27, 1970 to T. P. Flanagan; 4,411,954 issued December 6, 1983 to P. P. Puletti et al.; 4,136,699 issued January 30, 1979 to J. A. Collins et al.

In more detail, the natural oil is used with specific advantage in adhesives based on rubbery block copolymers. Conventional adhesives formulated with these block copolymers

suffer with respect to their inability to penetrate the substrates to be coated due to their relatively high viscosity at the temperatures at which the adhesives are applied. Use of the natural oils, and especially coconut oil, has been found to provide rubbery block containing adhesives characterized by penetration rates generally observed only with ethylene vinyl acetate based adhesive compositions.

The specific rubbery block polymers include the block or multi-block copolymers having the general configuration: A-B-A or A-B-A-B-A-B- wherein the polymer blocks A are non-elastomeric polymer blocks which, as homopolymers have glass transition temperatures above 20°C, while the elastomeric polymer blocks B are butadiene or isoprene or butadiene/isoprene which is partially or substantially hydrogenated. Further, they may be linear or branched. Typical branched structures contain an elastomeric portion with at least three branches which can radiate out from a central hub or can be otherwise coupled together.

The non-elastomeric blocks which generally make up 14 to 50% by weight of the block copolymer may comprise homopolymers or copolymers of vinyl monomers such as vinyl arenes, vinyl pyridines, vinyl halides and vinyl carboxylates, as well as acrylic monomers such as acrylonitrile, methacrylonitrile, esters of acrylic acids, etc. Monovinyl aromatic hydrocarbons include particularly those of the benzene series such as styrene, vinyl toluene, vinyl xylene, ethyl vinyl benzene as well as dicyclic monovinyl compounds such as vinyl naphthalene and the like. Other non-elastomeric polymer blocks may be derived from alpha olefins, alkylene oxides, acetals, urethanes, etc. Styrene is preferred.

The elastomeric block component making up the remainder of the copolymer is isoprene or butadiene which may or may not be hydrogenated as taught, for example, in US Patent No. 3,700,633. This hydrogenation may be either partial or substantially complete. Selected conditions may be employed for example to hydrogenate the elastomeric block while not so modifying the vinyl arene polymer blocks. Other conditions may be chosen to hydrogenate substantially uniformly along the polymer chain, both the elastomeric and non-elastomeric blocks thereof being hydrogenated to practically the same extent, which may be either partial or substantially complete.

Typical of the rubbery block copolymers useful herein are the polystyrene-polybutadiene-polystyrene, polystyrene-polyisoprene-polystyrene and e.g., polystyrene-poly-(ethylenebutylene)-polystyrene and polystyrene-poly-(ethylenepropylene)-polystyrene.

These copolymers may be prepared using methods taught, for example, in US Patent Nos. 5 3,239,478; 3,427,269; 3,700,633; 3,753,936; and 3,932,327. Alternatively, they may be obtained from Shell Chemical Co. under the trademarks Kraton 1101, 1102, 1107, 1650, 1652 and 1657; from Enichem under the Europrene Sol-T trade names; and from Firestone under the tradename Stereon 841 (formerly referred to as Stereon 840A). Also useful herein are the vinyl modified block copolymers such as Stereon 857 available from Firestone.

10 Other adhesive compositions may be prepared according to the invention using, as a base polymer, amorphous polyolefins or blends thereof. Adhesives based on these polyolefins generally contain the olefin at levels of about 10 to 50% by weight of the adhesive. Amorphous polyolefins are made by the stereospecific polymerization of polypropylene. Polymerization occurs in the presence of a catalyst comprising a  
15 coordination complex of a transition metal halide with an organometallic compound. The solid amorphous polypropylene has a softening point of about 150°C and a viscosity at 190°C of 1000 to 4500 mPa s. Suitable commercial products include Eastmans P 1010. Copolymers of amorphous polypropylene and ethylene (APE), butene (APB) and hexene (APH) are suitable as a base polymer, as are terpolymers of propylene, butene and  
20 ethylene (APBE). Commercial examples of APE include Rextac 2315 from Rexene, of APB including Rextac 2730 from Rexene and APBE include Vestoplast 750 and 708 from HÖls.

Ethylene containing polymers are also commonly used for disposable applications and can be utilized with the natural oil in accordance with the teachings of the invention.  
25 Thus ethylene is polymerized with 15 to 45% by weight of such copolymerizable monomers as vinyl acetate, N-butyl acrylate, propylene, methyl acrylate, methyl acrylic acid, acrylic acid, metallocene catalysed olefinic polymers and the like as well as mixtures thereof. Adhesives based on ethylene containing polymers generally contain these polymers in amounts of 10 to 50% by weight.

Blends of any of the above base materials, such as blends of ethylene vinyl acetate and atactic polypropylene may also be used to prepare the hot melt adhesive composition.

The tackifying resins useful in the natural oil containing adhesive compositions can be hydrocarbon resins, synthetic polyterpenes, rosin esters, natural terpenes, and the like. More particularly, and depending upon the particular base polymer, the useful  
5 tackifying resins may include any compatible resins or mixtures thereof such as (1) natural and modified rosins such, for example, as gum rosin, wood rosin, tall oil rosin, distilled rosin, hydrogenated rosin, dimerized rosin, and polymerized rosin; (2) glycerol and pentaerythritol esters of natural and modified rosins, such, for example as the glycerol  
10 ester of pale, wood rosin, the glycerol ester of hydrogenated rosin, the glycerol ester of polymerized rosin, the pentaerythritol ester of hydrogenated rosin, and the phenolic-modified pentaerythritol ester of rosin; (3) copolymers and terpolymers of natured terpenes, e.g., styrene/terpene and alpha methyl styrene/terpene; (4) polyterpene resins having a softening point, as determined by ASTM method E28-58T, of from about 80° to  
15 150°C; the latter polyterpene resins generally resulting from the polymerization of terpene hydrocarbons, such as the bicyclic monoterpene known as pinene, in the presence of Friedel-Crafts catalysts at moderately low temperatures; also included are the hydrogenated polyterpene resins; (5) phenolic modified terpene resins and hydrogenated derivatives thereof such, for example, as the resin product resulting from the  
20 condensation, in an acidic medium, of a bicyclic terpene and a phenol; (6) aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from about 70° to 135°C; the latter resins resulting from the polymerization of monomers consisting of primarily of olefins and diolefins; also included are the hydrogenated aliphatic petroleum hydrocarbon resins; (7) aromatic petroleum hydrocarbon resins and the hydrogenated  
25 derivatives thereof; and (8) alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof. Mixtures of two or more of the above described tackifying resins may be required for some formulations. Again, the amounts of tackifying agents utilized are



dependent on the raw materials and the properties desired in the final adhesive product. These amounts are generally well known in the art and will vary in the range of about 25 to 80% by weight with ranges of 40 to 60% being most typical.

For some applications where "environmentally friendly" products are especially  
5 desired, it may be particularly advantageous to use naturally occurring tackifiers such as sucrose benzoate or other materials derived from renewable resources such as terpenes.

Depending on the end use application, various plasticizing or extending oils are also present in the composition in amounts of 5% to about 25%, preferably 5 to 20%, by weight in order to provide wetting action and/or viscosity control. Similarly, small amounts,  
10 i.e. less than about 15% by weight of various petroleum derived waxes may also be added to impart fluidity in the molten adhesive and flexibility to the set adhesives, as well as to serve as a wetting agent for bonding cellulosic fibres. It will be recognized that the use of such synthetic oils or waxes may be detrimental to some of the desired end use properties and, hence, great care should be taken in the selection and use thereof.

15 It will be recognized that small amounts of other polymeric materials conventionally used in hot melt adhesives may also be used herein; however, care should be taken in selection of such polymers so as not to deleteriously affect the thermal stability or other properties of the adhesive. For example, if materials such as vinyl pyrrolidone are included within the adhesive composition, it is important that the levels be kept very low, i.e. less than  
20 about 5%, since higher levels would have a detrimental effect on the desired thermal stability.

An antioxidant or stabilizer may also be included in the adhesive compositions described herein in amounts of up to about 3% by weight. Among the applicable antioxidants or stabilizers are high molecular weight hindered phenols and multi functional  
25 phenols such as sulfur and phosphorous-containing phenols. Representative hindered phenols include: 1,3,5-trimethyl 2,4,6-tris (3,5-di-tert-butyl-4-hydroxy-benzyl)benzene; pentaerythritol tetrakis-3(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate; n-octadecyl-3,5-di-tert-butyl-4-hydroxyphenol)-propionate; 4,4'-methylenebis (2,6-tert-butylphenol); 4,4'-thiobis (6-tert-butyl-o-cresol); 2,6-di-tertbutylphenol; 6-(4-hydroxyphenoxy)-2,4-bis(n-octyl-thio)-

1,3,5-triazine; di-n-octadecyl 3,5-di-tert-butyl-4-hydroxy-benzyl-phosphonate; 2-(n-octylthio)-ethyl 3,5-di-tert-butyl-4-hydroxy-benzoate; and sorbitol hexa[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate].

The performance of these antioxidants may be further enhanced by utilizing, in conjunction therewith known synergists such, for example, as thiodipropionate esters and phosphites, particularly useful is distearylthiodipropionate. These stabilizers, if used, are generally present in amounts of 0.1 to 1.5 weight percent, preferably 0.25 to 1.0%.

Other additives conventionally used in hot melt adhesives to satisfy different properties and meet specific application requirements also may be added to the adhesive composition of this invention. Such additives include fillers, pigments, flow modifiers, dyestuffs, etc., which may be incorporated in minor or larger amounts into the adhesive formulation, depending on the purpose.

These hot melt adhesives may be prepared using techniques known in the art. Typically, the adhesive compositions are prepared by blending the components in the melt at a temperature of about 100 to 200°C until a homogeneous blend is obtained, approximately two hours. Various methods of blending are known and any method that produces a homogeneous blend is satisfactory. When formulated in accordance with higher levels of the natural oil in accordance with the preferred embodiment of the invention, the resulting adhesives are characterized by a viscosity of 3,000 mPa s or less at the application temperature of 130°C or less.

As a consequence, the adhesives of the present invention provide a durable bond to a nonwoven or tissue article and otherwise meet the unique requirements of the application (including flexibility, non-staining, machinable viscosity as well as thermal stability).

The adhesive product can be applied to a substrate such as a nonwoven article or tissue by a variety of methods including coating or spraying in an amount sufficient to cause the article to adhere to another substrate such as tissue, nonwoven, or an unrelated material such as a low density polyolefin or absorbent core materials or other conventionally employed substrates. Such applications also include the use of the adhesive to attach elastic to various substrates in the construction of disposable

nonwoven products. In addition to the other benefits achieved herein, it is also to be noted that the use of certain of the natural oils, such as coconut oil, may also provide soothing or other lubricating properties to the final construction thereby reducing some sources of skin irritation and rendering them more comfortable for the ultimate consumer.

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### EXAMPLES

In the following examples which are provided for illustrative purposes only, all parts are by weight and all temperatures in degrees Celsius unless otherwise noted.

In the examples, all adhesive formulations were prepared in a sigma blade mixer  
10 heated to 121°C by blending the components until homogeneous.

The adhesives were then subjected to various tests simulating the properties needed for successful commercial applications. As such, the adhesives are particularly suitable in nonwoven construction applications as well as in reinforcement of the absorbent materials used in the core of many disposable absorbent articles. Thus, the  
15 present invention is directed to a process for bonding tissue or nonwoven to similar or dissimilar substrates comprising the step of applying to at least one substrate a molten hot melt adhesive composition, said hot melt adhesive containing, as the plasticizing agent, a hydrogenated or non-hydrogenated natural oil selected from the group consisting of fatty acids containing about 6 to 22 carbon atoms and the pure fatty acid fragments thereof. In  
20 accordance with a preferred embodiment, the resulting adhesives are characterized by coating viscosities of 900 - 3 000 mPa s at 130°C so as to enable application at about 100°C while still maintaining a high level of heat stress resistance.

### Test Procedures

#### 25 Color Analysis

This test was undertaken by pouring color drops of approximately 4g and comparing them. The initial natural oil evaluation was undertaken by using the Lovibond machine and measuring Gardner colors.

Viscosity

Viscosity readings were taken on the Brookfield viscometer using spindle 9. Most were at 20 RPM, however this varied depending upon the viscosity. Readings were taken at 120, 140 and 160°C with a 10.5g sample.

5 Aged viscosity samples were taken at 140°C.

Thermal Stability

Thermal stability of the materials was determined by placing 50g of adhesive into a small glass jar and storing the loosely-covered jar in a forced air-recirculating oven at 10 180°C for periods up to 96 hours. The physical appearance of the aged sample was recorded, together with the amount of any char, gelled particles, or other evidence of oxidative degradation. Color analysis may also be performed as described above.

Needle Penetration

15 Needle penetration samples were prepared by pouring molten hot melt into ring shaped moulds. These were then left for 24 hours until the adhesive had solidified completely. The test involves a needle being pushed into the sample by a fixed force of 0.49N for 5 seconds. The distance that the needle has penetrated is recorded in units of 10 tenths of a mm.

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Softening Point

Small sample cups are filled with hot melt adhesive and left for 24 hours. The Mettler softening point machine was then used to record this range. The adhesive drops at its softening point and passes through the light source causing the reading to be 25 displayed.

Staining Test

4g of adhesive was placed between 2 sheets of white paper. Pressure was applied and left at 40°C for 24 hours. Observations were noted.

Odor

Odor analysis was recorded by a panel of twelve judges. The odor was rated on a scale of 1 to 7 with 1 being the best and 7 the worst.

5 Tensile Test

- Tensile testing was performed on cross sections of the adhesive. A molten mass of the adhesive was poured into a silicone rubber mould having central dimensions of 10mm length and 12.5mm width and end dimensions of 25 x 25mm. A strip of silicone release paper is placed over the adhesive and compressed with a smooth lead weight.
- 10 The sample is allowed to solidify and removed from the mould when completely cooled. Both ends of the moulded adhesive specimen are covered with tape to prevent sticking to the jaws of the Instron. The thickness of the centre of the sample is measured with a micrometer. The tensile strength of the specimen is then tested using an Instron tensile tester. The maximum load can be identified from a plot of load (force) vs elongation of the
- 15 specimen. Stress at maximum load is measured as maximum load/area. Strain at maximum load is measured as the extension at maximum load/original length. Stress at break is the final strength of the adhesive just before fracture calculated as load/area just before fracture. The procedure also provides a measurement of % elongation which is the % stretch of the hot melt, e.g. 500% elongation is 5 times the original length.
- 20 Young's modulus (modulus of elasticity) is obtained from the slope of the least squares fit straight line, made through the steepest linear region of the testing curve. High values indicate good elasticity and low values indicate poor elasticity.

Bond Strength

- 25 The adhesive is applied by spiral spray/slot coating using a Meltex coater onto polyethylene substrate and the non-woven is then immediately laminated therein. The temperature and air pressures are adjusted to give a coating weight between 6 and 10 grammes per square metre at temperatures of between 100 and 130°C. The coating width is about 4cm. The bonds are conditioned at 22°C; 50% RH for 24 hours and are cut

into 25mm-width strips before testing on an Instron tensile testing machine. Test parameters are 300mm/min speed and test results are given as 180° peel strength per 25mm bond width and are typically quoted in grammes.

5 Heat Resistance

The heat resistance is measured as the time taken for a 100mm bond length to 180° peel when held at 40°C:

EXAMPLE 1

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The following example illustrates the effect of various natural oils as plasticisers in block copolymer based hot melt adhesive compositions. All the formulations evaluated in Table I, comprised 17 parts Stereon 841, a polystyrene-polybutadiene block copolymer from Firestone, 58.7 parts Zonarez 1115, a terpene tackifier from Arizona Chemical, 0.3

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parts of a hindered phenolic antioxidant stabilizer and 24 parts of the oil as indicated.

Table I

Formulation	A	B	C	D	E	F	G
Oil	Enerpar Paraffinic Oil	Deodorized Coconut Oil	Coconut Oil	Deodorized Hard Soya Oil	Soya Oil	Sunflower Oil	Naphthenic Process
Viscosity /mPa s							
110°C	10,900	8,100	8,700	9,900	8,100	7,900	35,600
130°C	2,600	2,100	2,750	3,200	2,400	2,500	12,400
150°C		1,050	1,100	1,200	1,100	1,100	2,550
SPT/°C	111.5	80	77.8	86.1	77.9	878.7	110.9
Needle Penetration	49	86	79	26	97	86	36
Odor	3	2	1	4	6	5	7
Color & appearance	cream/ opaque	pale yellow/ transparent	cream/ opaque	cream/ opaque	yellow/ transparent	yellow/ transparent	caramel/ orange

As the results show, the addition of the natural oils provided excellent plasticizing effects. Thus, the softening points of the formulations prepared with the natural oil were substantially lower (77-86°C) compared to the 111 and 110°C of those prepared with conventional paraffinic (Enerpar M 1930 BP) and naphthenic oils (Catanex 956 from Shell). Moreover, the needle penetrations at 25°C with the natural oils were much higher (i.e. the products were softer) than with traditional mineral oils, another indication of the excellent plasticizing effects of the natural oils. Further, the viscosity of the formulations at 130°C was much lower compared to the same formulation containing paraffinic or naphthenic oils. The rheological analysis of the formulations A to G revealed significant differences in the position and height of the loss tangent peak (tan delta), together with a variation in the plateau value of the dynamic complex modulus ( $G^*$ ). The natural oils significantly lower the tan delta peaks indicating that the adhesives have much lower glass transitions ( $T_g$ ) than the adhesives using either the paraffinic or naphthenic oils i.e., tan delta peak for C is 24°C whilst for A, tan delta peak is 28°C and for G, tan delta peak is 32°C. In addition to the lowered  $T_g$ , the value of the tan delta at service temperatures (20-40°C) is significantly lower than that of the mineral oils indicating that, whilst the actual modulus is lower, the contribution of elasticity to the complex modulus is higher i.e., softer products with higher amounts of cohesive strength. The final feature observed with the natural oils is a much lower crossover temperature indicating lower softening point as confirmed by the Mettler softening point values. Coconut oil is the preferred option as it has a superior balance of reduced  $T_g$ , complex modulus and crossover temperature although all of the natural oils show similar trends.

It is to be noted that the odor and thermal stability of the formulation based on coconut oil was significantly better as compared to the standard mineral oils and also the sunflower and soy bean oils, an indication that coconut oil is particularly preferred for use herein.



## EXAMPLE 2

This example show the effect of different tackifying resins in a standard block copolymer based hot melt adhesive prepared using coconut oil. In this example, a variety of aromatic modified resins of varying degrees of aromaticity were employed.

5 The formulations tested herein were prepared using the same raw materials and amounts as in Formulation C of Example 1, varying only the type of tackifying resin employed. In these formulations, Zonarez 1115 is a terpene resin available from Arizona Chemical; Escorez 5300 is a hydrogenated dicyclopentadiene resin from Exxon; Zonatac105L is a styrenated terpene resin from Arizona Chemical; ECR 179A is a styrenated C5 hydrocarbon resin available from Exxon; and Bevilite 62-107 is tall oil rosin ester from Arizona.

Table II

Formulation	1	2	3	4	5
Resin	Zonarez 1115	Escorez 5300	Zonatac 105L	ECR 179A	Bevilite 62-107
Viscosity /mPa s					
110°C	9,900	6,700	5,500	5,250	4,800
130°C	2,800	2,650	2,000	2,300	2,000
SPT/°C	79.5	65.4	60.3	61.5	60.8
Needle Penetration	84	92	186	214	188
Comments	more solid than rest	soft/sticky	COLD FLOW	COLD FLOW	very soft & sticky

15 The results presented in Table II illustrate the softening effect, as evidenced by the penetration figures above 150, achieved by the use of the coconut oil in conjunction with the more the aromatic resins, (i.e. Formulations 3, 4 and 5). In the latter formulations, however there was some tendency for cold flow which tendency could be overcome by the use of the less aromatic resins (e.g. Zonarez 1115 terpene resin and Escorez 5300 hydrogenated dicyclopentadiene resin). These formulations (1 and 2 also gave excellent pressure sensitive adhesive properties with no cold flow and needle penetration values of 80-90.

## EXAMPLE 3

This example illustrates the use of the coconut oil in formulations based on styrene-butadiene-styrene block copolymers (Stereon 841) and styrene isoprene styrene block polymers (Vector 4411) in comparison to conventionally employed paraffinic oil (Enerpar M  
5 1930). In addition to the raw materials listed in the Table, all formulations contained 0.4 parts of a stabilizer system. ESBO is epoxidized soy bean oil supplied by Ciba.

Table III

	6	7	8	9	10
Formulation	20 Stereon 841 63 Zonarez 1115 15 Coconut Oil	20 Stereon 841 65 Zonarez 1115 18 ESBO	20 Stereon 841 65 Zonarez 1115 15 Enerpar	17 Vector 4411 63 Zonarez 1115 20 Coconut Oil	17 Vector 4411 63 Zonarez 1115 20 Enerpar
Viscosity/mPa s					
110°C	57,650			30,200	93,000
130°C	10,339	13,690	24,200	3,050	6,100
150°C	3,350	4,645	8,500	900	
Viscosity after 72H @ 180°C					
150°C	1,150	2,300	3,600	300	500
Needle Penetration					
		14	10	85	40
SPT/°C					
	98.9	97.5	115.4	91.2	116.4
Tensile data					
Stress at max load	91.71	144.9	45.64	59.89	115.4
Stress at break	43.7	77.19	68.37	53.09	115.1
Stress at 100%strain	63.88	129.1	129.1	6.874	13.62
Young's Modulus	690.2	1391	1350	51.66	136.1
Odor	acceptable	good	poor	acceptable	poor
Comments	no skin	no skin	skin on surface higher viscosity	lower viscosity no skin	cloudy

As was observed preciously, the formulations containing coconut oil gave lower viscosity, lower softening point and softer products compared to standard paraffinic oil. This combination of properties renders the adhesives ideally suited for very low application temperature uses such as in disposable constructions where the adhesive is applied to heat sensitive substrates. Thermal stability and resistance to skinning are also noticeably improved with the use of the natural oils.

#### EXAMPLE 4

In this example, formulations based on coconut oil were compared with a standard commercially available low viscosity hot melt adhesive formulation containing 35% of a styrene-butadiene styrene block copolymer, 25% white paraffin oil and 40% hydrocarbon resin (Control).

In the example, Sol T166 is a styrene butadiene styrene block copolymer available from Enichem.

Table III

	6	7	8	9	10
Formulation	20 Stereon 841 65 Zonarez 1115 15 Coconut Oil	20 Stereon 841 65 Zonarez 1115 15 ESBO	20 Stereon 841 65 Zonarez 1115 15 Enerpar	17 Vector 4411 63 Zonarez 1115 20 Coconut Oil	17 Vector 4411 63 Zonarez 1115 20 Enerpar
Viscosity/mPa s					
110°C	57,650	13,690	24,200	30,200	93,000
130°C	10,339	4,545	8,500	3,050	6,100
150°C	3,350			900	
Viscosity after 72H @ 180°C					
150°C	1,150	2,300	3,600	300	500
Needle Penetration	22	14	10	85	40
SPT/°C	88.9	97.5	115.4	91.2	116.4
Tensile data					
Stress at max load	91.71	144.9	45.64	69.89	115.4
Stress at break	43.7	77.19	68.37	53.09	115.1
Stress at 100%strain	63.88	1391	129.1	6.874	13.62
Young's Modulus	690.2		1350	51.66	136.1
Odor	acceptable	good	poor	acceptable	poor
Comments	no skin	no skin	skin on surface higher viscosity	lower viscosity no skin	cloudy

The results presented in Table IV show that the formulations based on coconut oil and terpene resin are excellent compared to the commercial control which has a similar viscosity to formulations 11 and 12 at suitable application temperatures.

When the bonds were aged up to 4 weeks at room temperature and also at  
5 elevated temperatures the bond strengths of the coconut oil containing formulations remained stable for the entire testing period.

#### EXAMPLE 5

This example shows the effect of the coconut oil in a conventional hot melt  
10 formulation used for garment attachment in feminine hygiene applications.

In this example, Stereon 857, a vinyl modified styrene-butadiene block copolymer available from Firestone is used.

Table IV

Formulation	11	12	13	14	Control
Formulation:	17 Stereon 841 58.7 Zonarez 1115 24 Coconut Oil	17 Vector 4111 63 Zonarez 1115 20 Coconut Oil	17 SolT 166 58.7 Zonarez 1115 24 Coconut Oil	17 SolT 166 58.8 Zonarez 1115 14 Coconut Oil	
Viscosity/mPa s					
110°C	7,900	5,000	8,400	16,300	10,500
130°C	2,400	1,900	3,250	4,000	2,650
150°C	1,100	850	1,550	1,700	1,100
Needle Penetration	65	153	73	62	140
SPT°C	77.8	64.3	74.2	86.8	82.6
Tensile data					
Stress at max load	21.91	15.8	26.37	36.29	28.91
Stress at break	3.281	4.352	14	11.44	3.72
Stress at 100% strain	10.64	2.318	11.14	10.05	1.746
Young Modulus	40.81	4.674	43.12	51.45	4.574
Initial Bond Strength @23°C /g	81.78 (+/-5.98)	160.1 (+/-15.1)	240.6 (+/-17.7)	N/T	43.36 (+/-7.55)
Bond Strength after 1 week @23C /g	82.53 (+/-7.99)	136.7 (+/-7.7)	157.4 (+/-5.9)	N/T	46.31 (+/- 7.81)
after 1 week@40C /g	104.70 (+/-13.68)	233.9 (+/-17.7)	199.5 (+/-31.3)	N/T	87.32 (+/-10.48)
after 2 weeks@40C /g	94.33 (+/-7.36)	209.5 (+/-5.8)	184.2 (+/-23.6)	N/T	79.01 (+/-7.18)
after 4 weeks@40C /g	78.64 (+/-4.79)	236.2 (+/-41.6)	128.0 (+/-10.7)	N/T	97.9 (+/-8.8)
Heat Resistance @ 40°C /hours	1.5	4.12	0.45		1.15
72H Stability	Good	Good	Good		Good
Viscosity @ 130°C/mPa s	600	400			400
Comments	More flexible and tacky to Formulation 6	Much more flexible and tacky to Formulation 9	Higher tensile strength to Formulation 11	Slightly tackier to Formulation 13	

The results presented in Table V indicate that the properties of the nonwoven adhesive may be substantially modified by the use of natural oils in combination with paraffinic oils, as well as by themselves.

5           The results present in Table V clearly show that the addition of coconut oil has a positive effect upon the physical properties of the adhesive. This effect is cumulative, since the formulation containing only coconut oil gave a soft adhesive with the benefits already described herein whilst the 2:1 and 1:1 M1930:coconut oil blends gave good adhesive performances with heat resistance results improving from the rather low 0.54 hours with the  
10 neat coconut oil up to a more respectable 10.25 hours which could still be sufficient for certain applications. The peel results show again that the addition of coconut oil has a cumulative effect, more coconut oil giving increased simulated peel values. The open time results were very promising with the addition of coconut oil almost doubling the open time. These latter values compare favourably with typical EVA positioning formulations. Unlike the  
15 the peel and physical properties the effect coconut oil had on the open time was not cumulative and so it should be possible to optimise a formulation to obtain a balance which retains the increased peel and better physical properties.

Samples of the adhesives prepared above were set aside for aging. After one month, no oil migration was observed.

20

#### EXAMPLE 6

This example illustrates the use of various tackifying resins in coconut oil containing hot melt adhesives based on the Vector 4111 polymer. All formulations contained 17 parts Vector 4111, 20 parts Coconut oil, 0.4 parts of a stabilizing system and  
25 63 parts of the indicated tackifying resin.



Table V

	15	16	17	18	19
Formulation	22 Stereon 857 54.5 ECR 179A 23.5 Enerpar 0 Coconut Oil	22 Stereon 857 54.5 ECR 179A 0 Enerpar 23.5 Coconut Oil	22 Stereon 857 54.5 ECR 179A 11.75 Enerpar 11.75 Coconut Oil	22 Stereon 857 54.5 ECR 179A 7.8 Enerpar 15.7 Coconut Oil	22 Stereon 857 54.5 ECR 179A 15.7 Enerpar 7.8 Coconut Oil
Viscosity/mPa s	6,400 1,700	4,000 1,200	3,700 1,100	3,400 1,100	3,700 1,100
Needle Penetration	87	114	98	108	95
SPT/C	90.0	66.3	86.7	76.1	81.1
Tensile data					
Stress at max load	98 N/cm <sup>2</sup>	24	57	45	68
Stress at break	94 N/cm <sup>2</sup>	4	21	13	48
Stress at 500% strain	27 N/cm <sup>2</sup>	8	19	14	24
Young Modulus	17 N/cm <sup>2</sup>	4	11	9	12
Intermediate Peel Strength @ 23°C/g mm <sup>-1</sup> (Ave load)	151.7 (+/-12.2)			151.4 (+/-12.2)	151.1 (+/-30.32)
Simulation Peel Strength @ 23°C/g mm <sup>-1</sup> (Ave load)	287.7 (+/-9.0)			398.7 (+/-16.6)	321.9 (+/-25.1)
Heat Resistance @ 40°C /hours	72	0.54	8.5	2.48	10.25
Open time /s	1.2			2.2	2.2

The results presented in Table VI indicate that the best properties were obtained with the Zonarez 1115 pure terpene resin, a resin which is also based on a renewable resource and thus provides a very attractive adhesive for use in specific environmentally sensitive applications.

5

#### EXAMPLE 7

The following example illustrates the use of various pure fatty acid fragments and blends thereof in accordance with the teachings of the present invention. In all cases, the fatty acids were added in an amount of 20 parts to a formulation containing 0.4 parts of a  
10 stabilizing system, 17 parts Vector 4111, and 62.6 parts Zonarez 1115.

Table VII

Formulation	26	27	28	29	30
Fatty acid	pure C8	71%C8+29% C10	55%C8+45%C10	Pure C10	C8/C10/C18 (33% of each)
Viscosity /mPa s					
110°C	9,000	9,100	9,600	10,800	11,500
130°C	3,600	3,600	3,800	4,100	4,400
150°C	1,800	1,700	1,900	1,900	2,000
Needle Penetration					
0-5°C	37	33	36	33	9
23°C	133	130	121	120	76
40°C	flows	flows	flows	flows	180
SPT/C	65.9	67.7	68.2	70.3	76.8

The use of fatty acid fragments of natural oils can also give adhesives with desirable properties. The use of pure C8 and pure C10 fragments give higher viscosities than the coconut oil (compare with formulation 12) and are harder. Softening points are also increased but the formulations are still viable and are capable of modification by judicious blending of the fatty acid fragments and the natural oils.

## EXAMPLE 8

The adhesive formulations in the following example are characterized by higher viscosities at 130°C and are especially suitable for use in bonding elastic to nonwoven or polyolefin substrates. In the formulations, Hercules MBG217 is a hydrogenated hydrocarbon monomer tackifying resin; Europrene Sol TE 6414 is a Styrene Butadiene Styrene thermoplastic rubber from Enichem; Europrene Sol T 193B Styrene Isoprene Styrene thermoplastic rubber from Enichem;

Table VIII

	31	32
Zonarez 1115	54.7	47.7
Hydrogenated Coconut Oil	15	15
Antioxidant	0.3	0.3
Hercules MBG217	5	
Vector 4411	25	
Sol TE 6414		16.5
Sol T 193B		8.5
Zonatac L105		12
%Renewable Raws	69.7	71.1
Viscosity @ 130C (mPas)	18900	10100
Viscosity @ 160C (mPas)	2000	2500
Softening Point (C)	111	91.9
Needle Penetration (1/10 <sup>th</sup> mm)	33	47
Stress at Max Load (N/m <sup>2</sup> )	118	107
Stress at 500% Strain (N/m <sup>2</sup> )	35	27

**What is claimed:**

1. The process for bonding tissue or nonwoven to similar or dissimilar substrates comprising the step of applying to at least one substrate a molten hot melt adhesive composition, said hot melt adhesive containing, as the plasticizing agent, a hydrogenated or non-hydrogenated natural oil selected from the group consisting of fatty acids containing about 6 to 22 carbon atoms and the pure fatty acid fragments thereof.
2. The process of Claim 1 wherein the natural oil contains 10 to 14 carbon atoms.
3. The process of Claim 1 wherein the oil is coconut oil.
4. The process of Claim 1 wherein at least one substrate comprises an absorbent core.
5. A process for bonding tissue or nonwoven to similar or dissimilar substrates comprising the step of applying to at least one substrate a molten hot melt adhesive composition, said hot melt adhesive consisting essentially of a styrene containing rubbery block copolymer, a compatible tackifying resin and containing, as the sole plasticizing agent therefor, a hydrogenated or non-hydrogenated natural oil selected from the group consisting of fatty acids containing about 6 to 22 carbon atoms and the pure fatty acid fragments thereof.
6. The process of Claim 5 wherein the rubbery block copolymer is selected from the group consisting of polystyrene-polybutadiene-polystyrene, polystyrene-polyisoprene-polystyrene, polystyrene-poly-(ethylenebutylene)-polystyrene and polystyrene-poly-(ethylenepropylene)-polystyrene.

7. The process of Claim 5 wherein the rubbery block copolymer is present in an amount of 10 to 30% by weight of the adhesive.
8. The process of Claim 1 wherein the tackifying resin is selected from the group consisting of (1) natural and modified rosins; (2) glycerol and pentaerythritol esters of natural and modified rosins; (3) copolymers and terpolymers of natured terpenes; (4) polyterpene resins having a softening point, as determined by ASTM method E28-58T, of from 80° to 150°C; (5) phenolic modified terpene resins and hydrogenated derivatives thereof; (6) aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from about 70° to 135°C; (7) aromatic petroleum hydrocarbon resins and the hydrogenated derivatives thereof, and (8) alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof.
9. The process of Claim 1 wherein the tackifying resin is derived from a renewable resource.
10. The process of Claim 9 wherein the tackifying resin is sucrose benzoate.
11. The process of Claim 9 wherein the tackifying resin is a natural terpene.
12. The process of Claim 1 wherein the adhesive contains 10 to 50% by weight of an amorphous ethylene or polypropylene based polymer.
13. A process for bonding tissue or nonwoven to similar or dissimilar substrates comprising the step of applying to at least one substrate a molten hot melt adhesive composition, said hot melt adhesive containing, as the plasticizing agent, a hydrogenated or non-hydrogenated natural oil selected from the group consisting of fatty acids containing about 6 to 22 carbon atoms and the pure fatty acid fragments thereof; the resulting adhesive characterized by coating viscosities of 9 00 - 3,000 mPa s at 130°C so

as to enable application at about 100°C or lower while still maintaining a high level of heat stress resistance, wettability of the substrates, and excellent bond strengths.

14. A process for bonding tissue or nonwoven to similar or dissimilar substrates  
5 comprising the step of applying to at least one substrate a molten hot melt adhesive composition, said hot melt adhesive consisting essentially of a styrene containing rubbery block copolymer, a compatible tackifying resin and containing, as the sole plasticizing agent therefor, a hydrogenated or non-hydrogenated natural oil selected from the group consisting of fatty acids containing about 6 to 22 carbon atoms and the pure fatty acid  
10 fragments thereof; the resulting adhesive characterized by coating viscosities of 900 - 3 000 mPa s at 130°C so as to enable application at about 100°C while still maintaining a high level of heat stress resistance, wettability of the substrates, and excellent bond strengths.

15 15. A disposable absorbent product prepared by the process of Claim 1.

16. A disposable absorbent product prepared by the process of Claim 5.

17. A hot melt adhesive composition consisting essentially of a styrene containing  
20 rubbery block copolymer, a compatible tackifying resin and containing, as the sole plasticizing agent therefor, a hydrogenated or non-hydrogenated natural oil selected from the group consisting of fatty acids containing about 6 to 22 carbon atoms and the pure fatty acid fragments thereof.

25 18. A hot melt adhesive composition consisting essentially of a styrene containing rubbery block copolymer, a compatible tackifying resin and containing, as the sole plasticizing agent therefor, a hydrogenated or non-hydrogenated natural oil selected from the group consisting of fatty acids containing about 6 to 22 carbon atoms and the pure fatty acid fragments thereof; the resulting adhesive characterized by coating viscosities of

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900 - 3,000 mPa s at 130°C so as to enable application at about 100°C while still maintaining a high level of heat stress resistance, wettability of the substrates, and excellent bond strengths.



INTERNATIONAL SEARCH REPORT

International Application No  
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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C09J11/08 C09J153/02 C09J153/00 A61L15/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 368 141 A (H.B. FULLER COMPANY) 16 May 1990 see page 5, line 30 - line 35 see page 6, line 14 - line 19. see claim 1 ---	1,4-9, 11,13-18
A	US 5 120 781 A (JOHNSON JR.) 9 June 1992  see column 4, line 63 - column 5, line 5 see column 5, line 12 - line 16 see column 6, line 65 - column 7, line 40 --- -/--	1-9, 12-18

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Mazet, J-F

INTERNATIONAL SEARCH REPORT

International Application No  
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Week 8335 Derwent Publications Ltd., London, GB; AN 83-749779 XP002088658 "Hot melt adhesive composn. contg. block copolymer- of conjugated diene and vinyl aromatic hydrocarbon, adhesive resin, softening agent and stabiliser." &amp; JP 58 122940 A (ASAHI CHEM IND CO LTD) , 21 July 1983 see abstract</p>	1,5,6, 13,14,18
A	<p>--- GB 2 058 610 A (NICHIBAN CO. LTD) 15 April 1981 see page 1, line 62 - page 2, line 32</p>	1,2,5-8, 17
A	<p>--- WO 95 10576 A (H.B. FULLER) 20 April 1995</p>	
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